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FTIR (Fourier Transform Infrared) Transmission Spectrometry for the Nondestructive Determination of Ammonium and Sulfate in Ambient Aerosols Collected on Teflon Filters

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16. ABSTRACT

Fourier transform infrared transmission spectroscopy is used to analyze directly for sulfate and ammonium present in ambient aerosol particles deposited on Teflon filters. Integrated infrared peak areas for sulfate and ammonium are linearly related to x-ray fluorescence measurements for total sulfur. The detection limit, in terms of total sulfur, is 450 ng/m^3 using samples volumes of 21.6 m^3. The actual detection limit may be less since uncertainties of 5-8% occur in the x-ray fluorescence measurements and all sulfur may not be in the form of ammonium sulfate. In order to determine the influence of site-dependent variations in collected particles on the infrared measurement, samples from four widely different sites were analyzed.

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FTIR TRANSMISSION SPECTROMETRY FOR THE NONDESTRUCTIVE DETERMINATION OF AMMONIUM AND SULFATE IN AMBIENT AEROSOLS COLLECTED ON TEFLON FILTERS

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Abstract—Fourier transform infrared (FTIR) transmission spectrometry has been used to determine ammonium and sulfate in ambient aerosol particles collected on Teflon filters. Integrated absorbance as well as maximum absorbance values for ammonium and sulfate are linearly related to X-ray fluorescence measurements of total sulfur. Apparent detection limits of 1.4 $\mu g\,m^{-3}$ for sulfate and 0.5 $\mu g\,m^{-3}$ for ammonium (for sample volumes of 21.6 m^3) were estimated for samples from Topeka, Kansas; Portage, Wisconsin; Steubenville, Ohio; and Charlottesville, Virginia. The apparent detection limits were essentially independent of sample loading over the range of 0–20 $\mu g\,m^{-3}$ of total sulfur. The FTIR transmission measurements of these samples are very precise, e.g. repetitive measurements vary $\pm 0.2\%$ and blank variability is 0.13 $\mu g\,m^{-3}$ and 0.20 $\mu g\,m^{-3}$ in terms of sulfate and ammonium, respectively. Contributions to analytical uncertainty include 5–8% uncertainties in X-ray fluorescence measurements for total sulfur and the influence of unspecified site-dependent sample characteristics. The method offers the significant advantages of nondestructive analysis, no sample preparation, molecular speciation and rapid analysis.

Key word index: Fourier transform, ammonium, sulfate, infrared, particles, FTIR, aerosols, pollution.

INTRODUCTION

It has become increasingly obvious over the past few years that the presence of sulfur containing species in the atmosphere contributes to environmental and health related problems. Sulfur in atmospheric aerosols is usually present in the form of ammonium sulfate, which is often a major component of the fine particle fraction ($\leqslant 2.5\,\mu m$ aerodynamic diameter) (Lewis and Macias, 1980). Ammonium and sulfate are routinely measured as part of studies of visibility degradation, SO_2-to-sulfate conversion, transport and fate of aerosols and health effects (U.S.E.P.A.).

Ambient aerosol particles are typically collected on filter substrates by use of dichotomous virtual impactor samplers (Stevens *et al.*, 1978). One of the primary methods for elemental analysis of particles collected on filter substrates is X-ray fluorescence (XRF) (Jaklevic *et al.*, 1976). The nature of this technique requires the use of a filter material which contains minimal amounts of the elements of interest; Teflon filters fulfil this requirement. Although sulfur inferred from XRF is usually present as ammonium sulfate, in current practice direct sulfate and ammonium measurements are made separately after filter extraction of the water soluble particle components. Sulfate is determined by ion chromatography or colorimetry, while ammonium is determined by either ion chromatography or ion selective electrode (Mulik *et al.*, 1976). These methods suffer from the fact that they are destructive, require a tedious extraction procedure, and may alter the chemical composition of the species of interest. The existence of these disadvantages has stimulated an interest in investigating alternative (nondestructive) methods for the quantification of NH_4^+ and SO_4^{2-}.

Recent efforts in our laboratories have concentrated on the development of nondestructive spectroscopic techniques for the characterization of aerosol particles collected on filter substrates (Röhl *et al.*, 1982). We wish to report here the application of Fourier transform infrared (FTIR) transmission spectrometry to the analysis of ambient aerosols collected on Teflon filters for NH_4^+ and SO_4^{2-}. Our goal was to develop an

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alternate analytical approach which: (1) is nondestructive, (2) requires no sample preparation, (3) provides information on molecular species and (4) is rapid and amenable to automation. In addition to investigating the applicability of the technique for routine quantitative analysis, the potential of infrared methods for rapid sample screening was considered.

Cunningham *et al.* (1974) reported FTIR spectra of ambient aerosols collected on filter substrates by incorporating the collected particles into KBr pellets. Subsequent work has shown spectral evidence for the presence of $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and H_2SO_4 in ambient particles, although accurate quantitative analysis of these mixtures is complicated by the gradual neutralization of acid sulfate to ammonium sulfate (Cunningham and Johnson, 1976). Gendreau *et al.* (1980) also reported the application of FTIR spectrometry to inorganic speciation in collected atmospheric particles. Their results pertain to samples of fly ash from coal- and oil-fired power plants which were prepared by pressing into KBr pellets. Miller and Jacobsen (1978) presented data obtained by direct FTIR spectrometric analysis of field-loaded filters and documented the transmission characteristics of commonly used filter types. Teflon was found to be the material best suited for infrared measurements. These previous reports demonstrate how the advantages inherent in commerical FTIR systems, i.e. spectral multiplexing, high optical throughput, precise wavelength (wavenumber) control and computerized data handling, can be applied to aerosol particle analysis. In addition, infrared data provide direct molecular information, as opposed to the indirect evidence inferred from elemental analysis (e.g. by XRF).

Surprisingly, the FTIR technique has not been applied to routine determinations of molecular species in ambient particles. Two possible reasons are the opaqueness in the infrared of a number of filter types in current use and the availability of the sensitive, albeit destructive, routine analyses provided by existing methods. Another reason is the lack of evidence that particle size distributions and the variable nature of co-collected ambient particles do not affect the transmission results to such an extent that accurate and precise measurements become impossible. In this paper, experimental results on samples from four particle collection sites are presented in order to estimate the extent of the combined effects mentioned above.

EXPERIMENTAL

Samples were selected from a large set of archived samples maintained by the Inorganic Pollutant Analysis Branch, E.P.A., Research Triangle Park, NC. A large number of sites were available along with tabulated results of elemental analysis by XRF. The samples had been collected over 24-h sampling periods on Ghia type 501 (1-μm pore size) Teflon filters using Beckman Model 101 dichotomous samplers, resulting in a total air sampling volume of 21.6 m^3. The collection area of the filters was 7.97 cm^2. Only the fine particle fraction filters ($\leq$ 2.5-μm aerodynamic diameter) were analyzed since most of the ammonium sulfate is in this fraction. Sites were selected to be as different as possible based on subjective criteria including geographical location, elemental analysis results and range of particle loadings. The sites selected were Topeka, Kansas; Portage, Wisconsin; Steubenville, Ohio; and Charlottesville, Virginia.

All infrared transmission spectra were obtained over the spectral range 4000–550 cm^{-1} using an IBM 9195 FTIR spectrometer. This N_2-purged instrument is equipped with a globar source, Ge/KBr beamsplitter, and a deuterated triglycine sulfate (DTGS) detector as well as a LN_2-cooled mercury cadmium telluride (MCT) detector. The MCT detector (Infrared Associates, New Brunswick, NJ) was chosen for these experiments due to its high sensitivity ($D^* = 36.7 \times 10^9$ cm $Hz^{1/2}$ W^{-1}) and fast response time. All spectra were collected using a mirror velocity (VEL = 11) of 0.396 cm s^{-1}, (corresponding to an optical velocity of 1.582 cm s^{-1}), and signal-averaged for 128 scans. This resulted in a data collection time of approximately 30 s per sample. The time limiting factor in these experiments was the time required to completely purge the sample compartment between samples (typically 10 min). The spectra were obtained at a nominal resolution of 4 cm^{-1} before apodizing using the Happ–Genzel function. A zero filling factor of two was used to enhance the signal-to-noise ratio without appreciably degrading resolution. An open aperture was used to completely fill the filter membrane with the i.r. beam in order to compensate for variations in loading density and concentration of species on the filter. The loaded side of the filters was positioned facing the incident radiation. This configuration reduced light scattering effects due to the Teflon substrate.

The sample (filter) spectra were ratioed to a reference (open-beam) spectrum and then converted into absorbance files. The absorbance files were baseline corrected in order to convert them into a form more suitable for quantitative analysis. Determinations of ammonium were carried out by integrating the baseline corrected spectra over the 1500–1350 cm^{-1} spectral range to obtain peak area values. For comparison, peak height measurements were made at 1420 cm^{-1}. Sulfate was determined by first interactively subtracting a blank filter file from the sample filter files over the 700–550 cm^{-1} spectral region to remove an interference at 640 cm^{-1} due to the Teflon substrate. A blank filter was included in each set of field-loaded filters as part of the sampling protocol. The spectrum of the blank filter was compared to that of individually loaded filters of the same set and then scaled in amplitude until a suitable baseline was achieved. This process takes approximately 1 min per sample. Integrated peak areas were calculated for the baseline corrected, subtracted spectra over the 635–580 cm^{-1} spectral region. Peak height measurements at 615 cm^{-1} were also performed for these subtracted spectra. Baseline correction, interactive spectral subtraction, and peak integration were all done using the standard IBM software supplied with the 9195. Linear least squares fitting and confidence interval plots were generated using a Hewlett–Packard 9825A computer interfaced to a Hewlett–Packard 7225A plotter. Confidence intervals were determined using a two-tailed *t*-test (Acton, 1959).

RESULTS AND DISCUSSION

Representative spectra of ambient aerosol particles collected on a Ghia type 501 Teflon filter and of a blank filter from the same data set are shown in Fig. 1. The spectrum of the field-loaded filter exhibits features consistent with those found in our laboratory for artificially generated $(NH_4)_2SO_4$ aerosol particles collected on similar filter substrates. The absorption

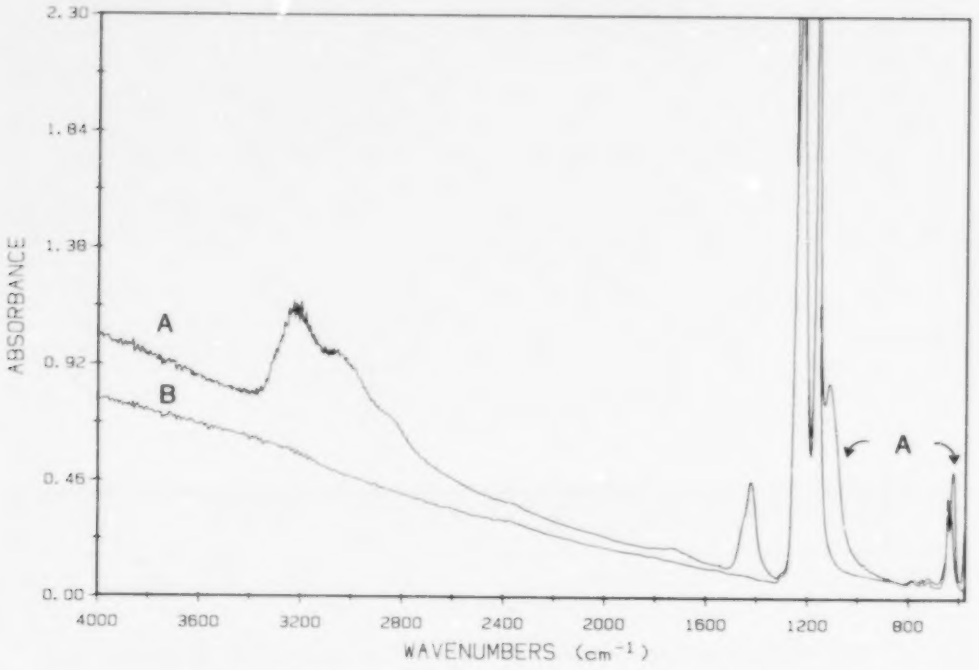

Fig. 1. FTIR spectra of (A) field-loaded Teflon filter and (B) blank Teflon filter.

bands due to ammonium and sulfate are assigned in Table 1. In addition to the absorption bands of the collected particles, bands due to the Teflon substrate in the region 1250–1150 cm^{-1} (C–F stretching) and at 640 cm^{-1} (C–F bending) are present. The spectra are also influenced by scattering of the incident radiation by the strands of Teflon of which the filter is composed, resulting in the smooth, monotonically decreasing extinction with decreasing wavenumber.

A difference spectrum, field-loaded sample minus scaled Teflon blank, is shown in Fig. 2. This spectrum illustrates the difficulty in completely subtracting out the strong Teflon bands in the 1250–1150 cm^{-1} region. This reduces the usefulness of the ν_3 (SO_4^{2-}) band at 1115 cm^{-1} for quantitative analysis. However, it is possible to compensate for the weaker Teflon band at 640 cm^{-1}, thus allowing the $\nu_4(SO_4^{2-})$ band at 615 cm^{-1} to be used. The ν_4 (NH_4^+) band at 1420 cm^{-1} is not interfered with by the Teflon bands and can be used for quantitative purposes without resorting to spectral subtraction techniques. Preliminary results in our laboratory using Ghia type 504 (2-μm pore size) Teflon filters indicated that problems associated with spectral subtraction were not as severe as for the Ghia type 501 (1-μm pore size) filters used in the study reported here. The absorbance values for the Teflon bands in the 1250–1150 cm^{-1} region do not exceed 1.0 for the 2-μm filters. Ideally, a blank spectrum of each filter should be obtained prior to field-loading to be used for subsequent subtraction. This procedure would most likely improve the usefulness of the strong $\nu_3(SO_4^{2-})$ band for quantitative analysis.

Table I. IR band assignments for NH_4^+ and SO_4^{2-} (Herzberg, 1964)

Peak maximum (cm^{-1})	Species	Normal mode
615	SO_4^{2-}	ν_4
1115	SO_4^{2-}	ν_3
1420	NH_4^+	ν_4
1700	NH_4^+	ν_2
2840	NH_4^+	$2\nu_4$
3050	NH_4^+	$\nu_2 + \nu_4$
3180	NH_4^+	ν_3

Figure 3 shows the linear least squares plot of integrated i.r. peak area for NH_4^+, over the spectral range 1500–1350 cm^{-1}, vs total sulfur as determined by XRF for all four data sets. A similar plot of integrated i.r. peak area for SO_4^{2-}, over the spectral range 635–580 cm^{-1}, vs total sulfur is shown in Fig. 4. The significant observation for both plots is that virtually all the data points from all four geographical locations fall near the same line. Table 2 presents calculated slopes, intercepts and correlation coefficients (r) for the linear least squares calculations for NH_4^+ and SO_4^{2-}, respectively. The values presented in Table 2 were determined using i.r. peak area (arbitrary units) as the dependent variable and total sulfur by XRF (in ng m^{-3}) as the independent variable. The total

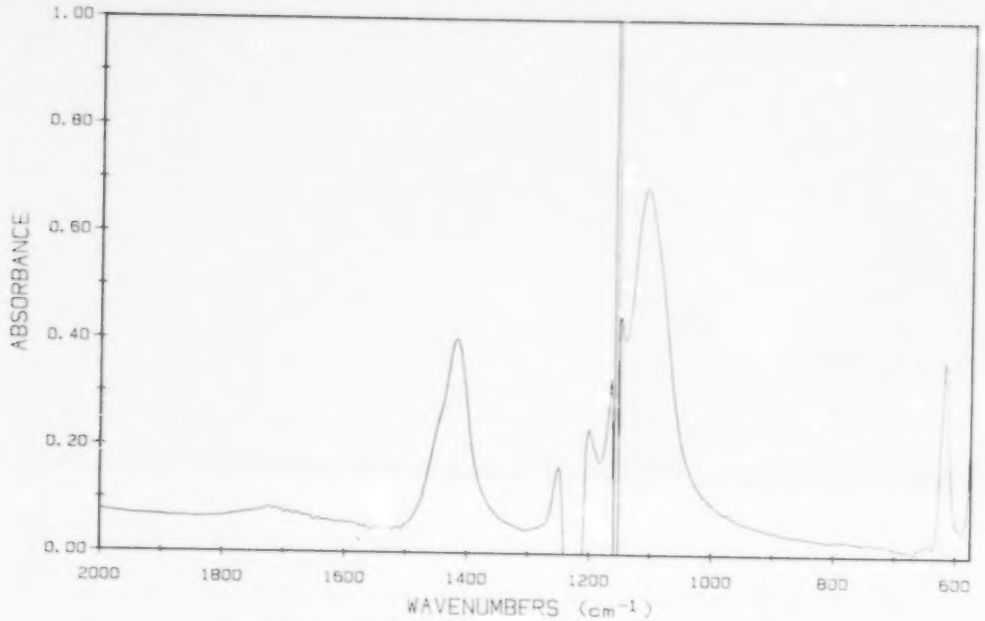

Fig. 2. FTIR subtraction spectrum (field-loaded Teflon filter minus scaled blank Teflon filter).

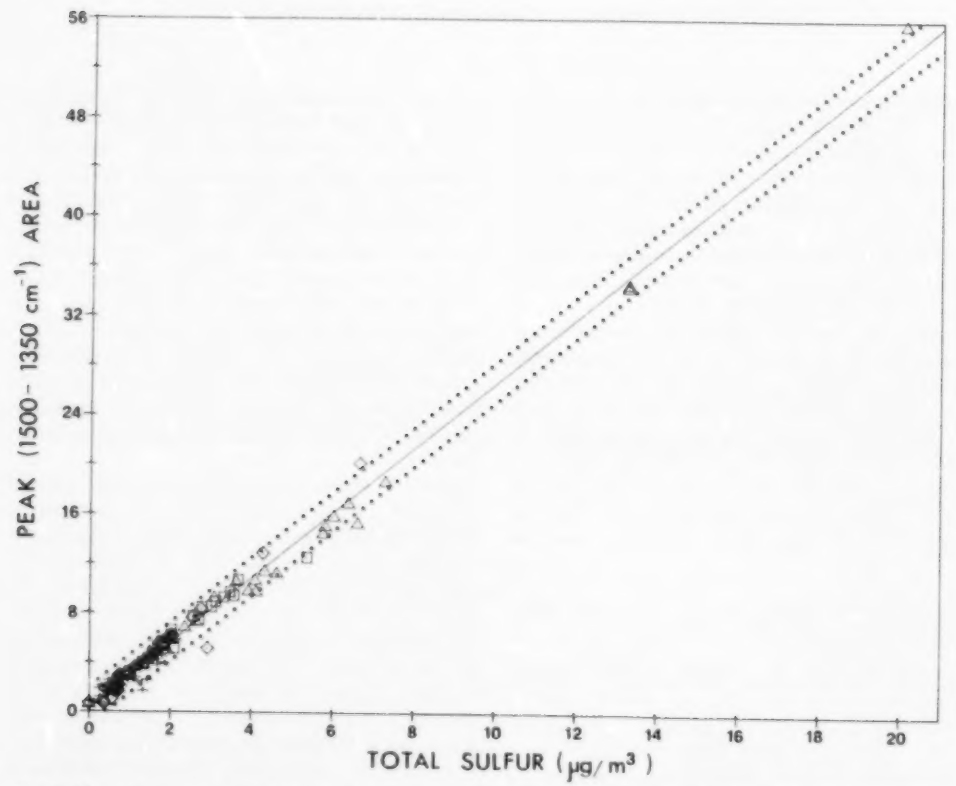

Fig. 3. Linear least squares plot of integrated FTIR peak (1500–1350 cm^{-1}) area for NH_4^+ vs total sulfur measured by XRF showing 95% confidence limits (. . . . .). Legend: Topeka (+), Portage (◇), Charlottesville (□) and Steubenville (Δ).

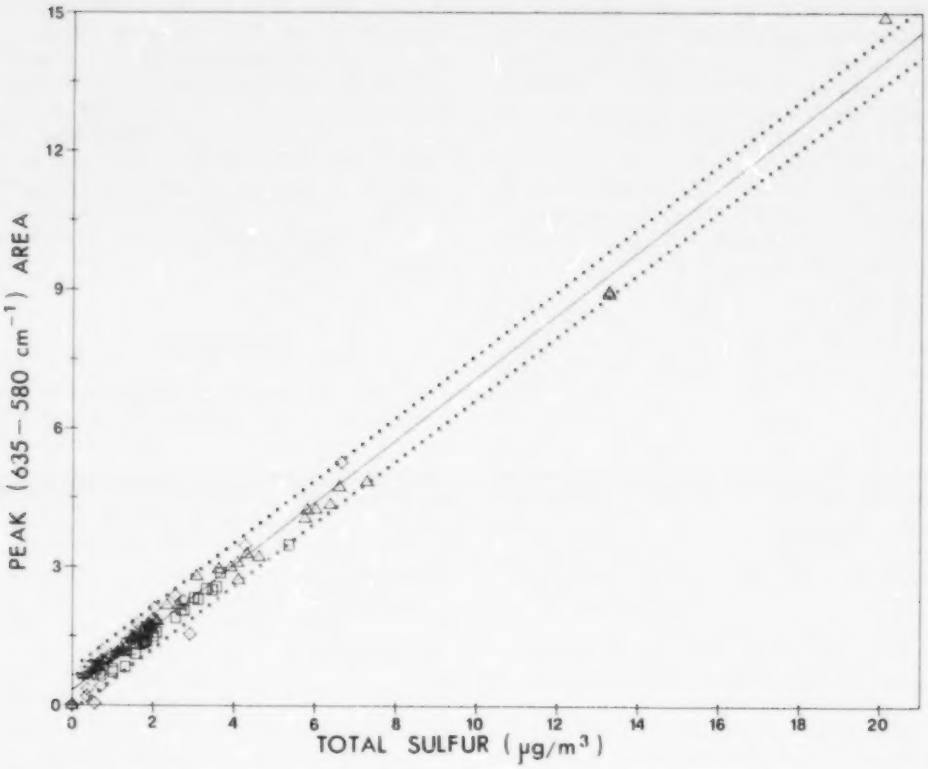

Fig. 4. Linear least squares plot of integrated FTIR peak (635–595 cm^{-1}) area for SO_4^{2-} vs total sulfur measured by XRF showing 95% confidence limits (. . . . .).

Table 2. Results of linear least square fitting calculations using integrated i.r. absorbance (in units of peak area) for NH_4^+ centered at 1420 cm^{-1} and for SO_4^{2-} centered at 615 cm^{-1} as the dependent variables and total sulfur by XRF (in $ng\,m^{-3}$) as the independent variable

Location	Number of filters	Slope × 1000*	Intercept × 10*	Correlation* coefficient (r)
Portage	27	2.90 ± 0.11(0.78 ± 0.04)	1.32 ± 2.23(2.31 ± 0.80)	0.96(0.94)
Topeka	33	1.78 ± 0.12(0.50 ± 0.04)	5.17 ± 0.99(5.24 ± 0.29)	0.88(0.87)
Steubenville	34	2.63 ± 0.03(0.68 ± 0.01)	2.28 ± 1.97(3.21 ± 0.62)	0.99(0.99)
Charlottesville	23	2.42 ± 0.11(0.67 ± 0.03)	1.01 ± 2.82(1.79 ± 0.63)	0.99(0.97)
Combined	117	2.69 ± 0.03(0.68 ± 0.01)	2.18 ± 0.91(3.18 ± 0.27)	0.99(0.98)

* Values for SO_4^{2-} in parentheses.

sulfur values, as determined by XRF, were assumed to be exact for the purpose of calculating the linear least squares fit. (In fact, a 5–8% relative standard deviation is associated with the XRF measurements.) This fact may have an influence on the apparent accuracy of the FTIR transmission technique as presented in this study, and may be partially responsible for the observed scatter in the least squares plot. However, the FTIR technique proved to be very precise, yielding highly reproducible results (±0.2%). The detection limits for SO_4^{2-} and NH_4^+ were based on measurements of a set of ten blank filters. The measurements for the blank filter set duplicated those used to obtain integrated peak area values from absorbance plots, resulting in ten peak area values. The scatter about the mean of these values in terms of the area value equal to three standard deviations was used as an estimate of the inherent detection limit. This detection limit, in terms of total sulfur, is 0.12 $\mu g\,cm^{-2}$ of filter area (0.35 $\mu g\,cm^{-2}$ of sulfate). Similarly, the estimated detection limit for ammonium is 0.53 $\mu g\,cm^{-2}$. For the collection volume involved in this study, these limits correspond to 0.13 $\mu g\,m^{-3}$ of sulfate and 0.20 $\mu g\,m^{-3}$ of ammonium. The detection limits measured in this way are significantly less than those obtained by projecting the intersection of a constant peak area value and the 95% confidence limits of the linear regression plots onto the abcissa. Since the 95% confidence limits are

approximately parallel to the linear regression line throughout the range of abscissa values, the detection limits, estimated in this way, are approximately equal to the x-intercept values for the 95% confidence intervals. The corresponding effective detection limits are 4 $\mu g\,cm^{-2}$ (1.4 $\mu g\,m^{-3}$) and 1.5 $\mu g\,cm^{-2}$ (0.5 $\mu g\,m^{-3}$) for sulfate and ammonium, respectively. The difference in detection limits estimated in these two ways is probably due to both the uncertainty in XRF values and to unspecified sample characteristics, the relative contributions of which have not been resolved with the current data set.

From the tabulated results it can be shown that for all the individual data sets, with the exception of the Topeka set, the calculated slopes relating i.r. peak area to total sulfur are within two standard deviations of the calculated combined slopes. These results suggest that the FTIR transmission technique is not severely affected by variations in site-dependent sample characteristics, and that a wide range of filter loadings can be analyzed successfully. Deviation of the calculated slopes for the Topeka data from those for the combined data sets is probably due to the fact that many of the data points (approximately one-fourth) for the Topeka set fall below the estimated detection limits for the technique. However, the Topeka data themselves fall within the 95% confidence limits calculated for the combined data sets. The inclusion of the three outlying data points of highest value leads to a distinctly non-uniform distribution of x- and y-values. However, the slopes, confidence intervals and correlation coefficients are almost identical with and without these three points. We chose to include these three data points in order to illustrate the wide dynamic range of the method. Analogous results were obtained by plotting peak heights vs total sulfur for both NH_4^+ and SO_4^{2-}.

One factor that has been suggested to affect the quantitative analysis of inorganic species is recrystallization (Gendreau *et al.*, 1980). For example, it was demonstrated that changes in the hydration state of $CuSO_4$ caused significant changes in the i.r. spectrum. In order to investigate these effects on field-loaded filters, one field-loaded filter was exposed to a 100% relative humidity environment for 24 h. A spectrum was collected immediately after removal from the humidity chamber and compared to a spectrum obtained prior to the exposure. The filter was then stored in a desiccator over Drierite for 24 h and a third spectrum was acquired. The three spectra were found to be nearly identical with the exception of slight peak broadening for the exposed sample. Peak areas for the region 1500–1350 cm^{-1} for the exposed and recrystallized sample were calculated to be within ± 3% of the initial spectrum. This is outside the error limits for repetitive measurements performed sequentially without alteration of the sample (± 0.2%) and suggests a small, but real, difference in the absorption spectra. No evidence of bound water was found.

Figure 5 shows the plot of peak (635–580 cm^{-1}) area for SO_4^{2-} vs peak (1500–1350 cm^{-1}) area for NH_4^+. This plot indicates a direct correlation between measured SO_4^{2-} and NH_4^+. This, along with the band assignments for the measured spectra, is consistent with the conclusion that all the SO_4^{2-} is in the form of $(NH_4)_2SO_4$ for the archived samples. This will not in general be the case when recently collected samples are analyzed, since un-neutralized (acid) sulfate can be expected to be present. In this case, appropriate reinterpretation of the spectra would be necessary, possibly allowing a determination of the degree of acidity.

CONCLUSIONS

We have demonstrated the applicability of FTIR transmission spectrometry to the quantitative determination of ammonium and sulfate in ambient particles collected on Teflon filters. Samples from four different geographical locations were analyzed for both NH_4^+ and SO_4^{2-}. Integrated peak areas for both species were plotted vs total sulfur obtained from XRF measurements. The slopes of these plots for the different sites were within narrow 95% confidence limits, suggesting that the variability (e.g. in particle size, matrix effects and recrystallization) of aerosols collected at different sites does not severely limit the validity of the results. One factor that could limit the general applicability of the method is the spectral interference of the NO_3^- (ν_3) absorption band at 1337 cm^{-1} with the determination of NH_4^+. The most likely nitrate present, ammonium nitrate, decomposes during and subsequent to collection if no precautions are taken (Johnson *et al.*, 1981). Residual nitrate can be identified by an independent measurement at 830 cm^{-1} (ν_2). A limiting factor for the determination of SO_4^{2-} is the alteration of the i.r. spectrum, in the region of sulfate absorption, when unneutralized sulfate is present (Cunningham and Johnson, 1976). However, the acid sulfate is usually neutralized subsequent to collection by reaction with ammonia in the ambient air. Neither of these factors significantly affected our results since all of the samples were drawn from archives.

The apparent detection limits for both sulfate and ammonium are one or two orders of magnitude higher than the corresponding detection limits for ion chromatographic analysis. However, the FTIR detection limits (as determined in this study) are somewhat raised by the uncertainty in the XRF measurements. Thus, the detection limits presented should be considered upper limits. Even though the current estimated detection limit for sulfate is high compared to that of ion chromatography, it is lower than the average ambient sulfate loading collected at remote sites in the Ohio River Valley (Shaw and Paur, 1983), i.e. 18.5 $\mu g\,cm^{-2}$ per sample or 5–10 $\mu g\,m^{-3}$ for a sampling volume of 21.6 m^3. As noted earlier, pre-loading measurements on the filters are expected to improve the accuracy and precision of the data. We believe optimization of the technique is warranted since it

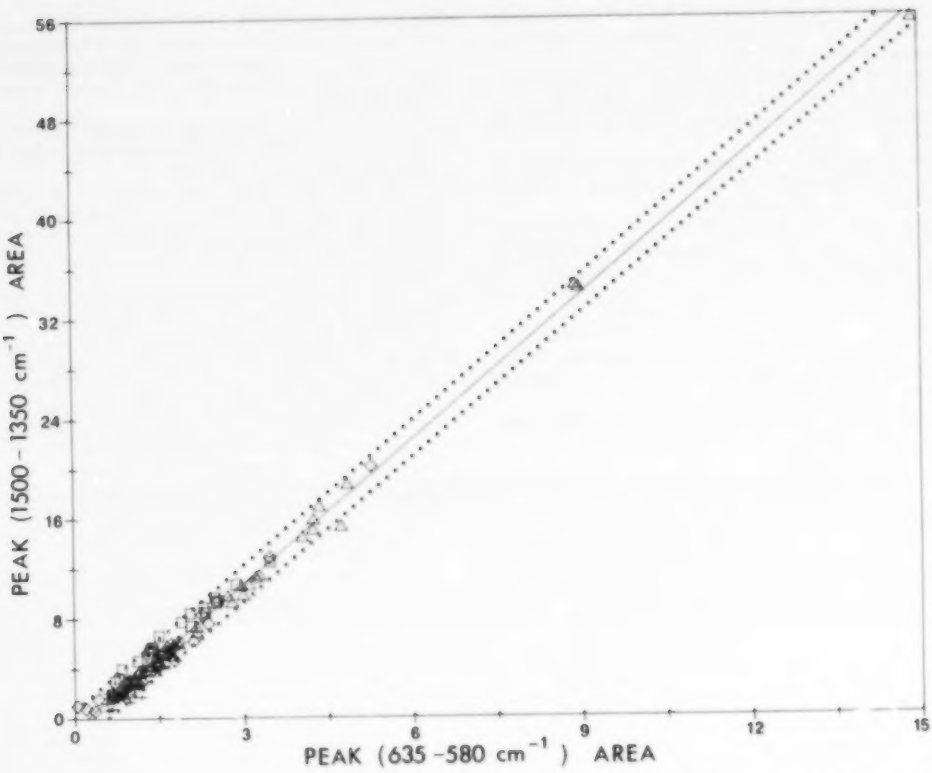

Fig. 5. Linear least squares plot of integrated FTIR peak (1500–1350 cm^{-1}) area for NH_4^+ vs integrated FTIR peak (635–595 cm^{-1}) area for SO_4^{2-} showing 95% confidence limits (. . . . .)

offers the significant advantages of nondestructive analysis, no sample preparation, rapid analysis, and independent measurements for NH_4^+ and SO_4^{2-}. The technique also yields highly reproducible quantitative results. In addition, the technique provides direct molecular information for the species of interest. This potentially would allow determination of the degree to which sulfates are balanced by ammonium in freshly collected aerosols.

In addition to being applicable to routine quantitative analysis, the technique also has the potential to be used for rapid screening. We have found that quantitative results can also be obtained by measuring i.r. peak heights as opposed to calculating peak areas for the species of interest. Such measurements could easily be made in the field using a more portable, less expensive instrument in order to screen samples to ensure adequate loading levels.

We have recently initiated a study in which freshly collected aerosols will be analyzed by FTIR transmission spectrometry, then subsequently analyzed by ion chromatography. This will provide an opportunity to investigate the effects of the presence of nitrate and unneutralized sulfate on the determination of ammonium and sulfate. Analyses by ion chromatography should enable more accurate detection limits to be determined for the FTIR technique. In addition, blank Ghia type 504 Teflon filters will be analyzed by FTIR transmission spectrometry prior to field-loading. Preloading analysis, and use of the less strongly absorbing filters, should facilitate the spectral subtraction procedure.

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Disclaimer—Although the research described in this article has been jointly conducted by the United States Environmental Protection Agency and Duke University, Durham NC, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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